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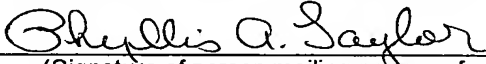
APPLICATION FOR UNITED STATES PATENT

LONG LIFE LUBRICATING OIL WITH
ENHANCED OXIDATION AND NITRATION RESISTANCE

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CROSS-REFERENCE TO RELATED APPLICATION(S):

Non-Provisional Application based on Provisional Application No. 60/419,745 filed October 18, 2002.

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LONG LIFE LUBRICATING OIL WITH
ENHANCED OXIDATION AND NITRATION RESISTANCE

5 **[0001]** This application claims the benefit of U.S. Provisional Application
No. 60/419,745 filed October 18, 2002.

FIELD OF INVENTION

10 **[0002]** The present invention relates to lubricating oils, especially gas engine
oils, having extended life as evidenced by a reduction in viscosity increase,
oxidation and nitration.

BACKGROUND OF INVENTION

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[0003] Gas fired engines are typically used in the oil and gas industry to drive
compressors that compress natural gas at well heads and along pipelines. These
engines are large, having up to 16 cylinders and often generate between 500 to
3000 HP. The nature of their use requires them to be able to run continuously
20 near full load conditions, shutting down only for maintenance such as for oil
changes. Under these operating conditions severe demands are placed on the
engine lubricant. Indeed, because the lubricant is subjected to a high
temperature environment, the life of the lubricant often is limited by oil
oxidation processes. Additionally, natural gas fired engines generate nitrogen
25 oxides (NO_x) that can limit lubricant life by oil nitration processes. Therefore,
gas engine operators are constantly seeking gas engine oils that have improved
resistance to oxidation and nitration.

[0004] In addition to controlling oxidation and nitration properties of a gas
30 engine oil it also is necessary to control the ash content of the oil because the

lubricant ash acts as a solid lubricant protecting the valve/seat interface of the engine. For this reason gas engine oils are classified according to their ash content. The classifications are:

<u>Ash Designation</u>	<u>Ash Level, wt% (ASTM D874)</u>
Ashless	Ash < 0.1%
Low Ash	0.1% < Ash < 0.6%
Medium Ash	0.6% < Ash < 1.5%
High Ash	Ash > 1.5%

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[0005] The ash level of the lubricant often is determined by its formulation components, with metal-containing detergents and metallic-containing antiwear additives contributing to the ash level of the lubricant. Gas engine manufacturers specify the appropriate lubricant ash level for correct operation of a given engine. Thus, manufacturers of 2-cycle engines often specify use of an ashless oil. Manufacturers of 4-cycle engine may specify low, medium or high ash depending upon the level required for engine cleanliness and durability.

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[0006] As is known in the art, additives are used in lubricants to perform numerous functions. For example, some are antioxidants, some are friction modifiers; and some are extreme pressure agents. Indeed some additives perform more than one function. Also as is known in the art additives will lose their effectiveness if they are improperly combined. Therefore, extreme care must be exercised in combining various additives to assure both compatibility and effectiveness. For example, some friction modifiers affect metal surfaces differently than antiwear agents do. When both are present, friction-reducing and antiwear additives may compete for the surface of the metal parts which are subject to lubrication. This competition can produce a lubricant that is less effective than is suggested by the individual properties of the additive components.

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[0007] Accordingly, the components of a gas engine lubricant need to be selected to meet the specified ash level and to provide, among other functions, a high level of oxidation and nitration resistance. Whether selected components and their amounts can be balanced to meet desired specification is not *a priori* predictable.

SUMMARY OF INVENTION

[0008] Simply stated the present invention relates to a lubricating oil, especially useful as a gas engine oil, comprising a major amount of a base oil of lubricating viscosity; effective amounts of a mixture of neutral and overbased metallic detergents; and, a minor amount of at least one trinuclear molybdenum compound.

[0009] The lubricant composition of the invention has extended life as evidenced by reductions in oxidation and nitration relative to commercial and reference oils and may also be compatible with other standard additives used in formulating commercial lubricating compositions.

DETAILED DESCRIPTION OF INVENTION

[0010] The lubricant compositions of the present invention include a major amount of a base oil of lubricating viscosity. Suitable base oils include natural and synthetic oils and mixtures thereof in API Categories I, II and III, and having a kinematic viscosity of about 9 to 13 cSt at 100°C.

[0011] The metallic detergent contained in the composition of the invention is a mixture of neutral and overbased metal sulfonates, phenates and

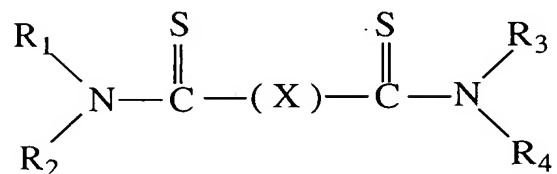
alkylsalicylates. The metals may be alkali and alkaline earth metals and preferably are alkaline earth metals, especially calcium and barium. Examples of suitable neutral metallic detergents are calcium sulfonates and calcium alkylsalicylates having a TBN of from 10 to 100. Examples of overbased
5 metallic detergents are calcium phenates, sulphonates and alkylsalicylates having a TBN of 150 to 400. The amount of the neutral and overbased metallic detergent is chosen having regard to the desired TBN of the final product and especially having regard to the desired sulfated ash of the final product. Preferably the mixture of neutral and overbased metallic detergents is sufficient
10 to provide the composition with a sulfated ash in the range of about 0.2 mass % to about 2.0 mass %.

[0012] The compositions of the present invention also include a minor amount of at least one trinuclear molybdenum compound. A preferred trinuclear
15 molybdenum compound is represented by the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ where L represents independently selected ligands, n varies from 1 to 4, k varies from 4 to 7 and Q is selected from the group consisting of neutral electron donating compounds including water, amines, alcohols, phosphines and ethers and z ranges from 0 to 5. Such compounds and their method of preparation are
20 disclosed in great detail in U.S. Patent 6,232,276 B1 which is incorporated herein by reference. In the present invention L preferably is dithiocarbamate, n is 4, k is 7, Q is an electron-donating compound, and z is 0. The trinuclear molybdenum compound preferably constitutes from 0.1 vol % to about 2.0 vol % based on the total volume of the total lubricant composition.

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[0013] Optionally, the composition may contain an ashless dihydrocarbyl thiocarbamoyl in combination with the trinuclear molybdenum compound.

[0014] Suitable dihydrocarbylthiocarbamoyl compounds are represented by the formula



where R₁, R₂, R₃ and R₄ are the same or different and each represents an alkyl group of 3 to 30 carbon atoms, X represents S, S-S, S-(CH₂)_yS, S-CH₂CH₂(CH₃)-S and y is an integer of 1 to 3.

[0015] Preferably the combined materials will constitute from about 0.1 vol % to about 2.0 vol % based on the volume of the total lubricant composition; however, the amount of dihydrocarbyl thiocarbamoyl will not exceed about 1.90 vol %.

[0016] The fully formulated oil may contain additional, typical additives known to those skilled in the industry, used on an as-received basis.

[0017] Thus, the fully formulated oil may contain dispersants of the type generally represented by succimides (e.g., polyisobutylene succinic

acid/anhydride (PIBSA)-polyamine having a PIB moiety molecular weight of about 700 to 2500). The dispersants may be borated or non-borated. The dispersant can be present in the amount of about 0.5 to 8 vol%, more preferably in the amount of about 1 to 6 vol%, most preferably in the amount of about 2 to 4 vol%.

[0018] Antioxidants may be of the phenol (e.g., o,o'-ditertiary alkyl phenol such as ditertbutyl phenol), or amine (e.g., dialkyl diphenyl amine such as

dibutyl, octyl buty, or dioctyl diphenyl amine) type, or mixtures thereof. More preferably, the antioxidants will be hindered phenols, or aryl amines which may or may not be sulfurized. Antioxidants can be present in the amount of about 0.05 to 2.0 vol%, more preferably in the amount of about 0.1 to 1.75 vol%, most preferably in the amount of about 0.5 to 1.5 vol%.

[0019] Metal deactivators may be of the aryl thiazines, triazoles, or alkyl substituted dimercapto thiadiazoles (DMTD's), or mixtures thereof. Metal deactivators can be present in the amount of about 0.01 to 0.2 vol%, more preferably in the amount of about 0.02 to 0.15 vol%, most preferably in the amount of about 0.05 to 0.1 vol%.

[0020] Antiwear additives such as metal dithiophosphates (e.g., zinc dialkyl dithiophosphate, ZDDP), metal dithiocarbamates, metal xanthates or tricreylphosphates may be included. Antiwear additives can be present in the amount of about 0.05 to 1.5 vol%, more preferably in the amount of about 0.1 to 1.0 vol%, most preferably in the amount of about 0.2 to 0.5 vol%.

[0021] Pour point depressants such as poly(meth)acrylates, or alkyl-aromatic polymers may be included. Pour point depressants can be present in the amount of about 0.05 to 0.6 vol%, more preferably in the amount of about 0.1 to 0.4 vol%, most preferably in the amount of about 0.2 to 0.3 vol%.

[0022] Antifoamants such as silicone antifoaming agents can be present in the amount of about 0.001 to 0.2 vol%, more preferably in the amount of about 0.005 to 0.15 vol%, most preferably in the amount of about 0.01 to 0.1 vol%.

[0023] Viscosity index Improvers (VII's) may be any polymer which imparts multifunctional viscosity properties to the finished oil, including materials such

as olefin copolymers, polymethacrylates, styrene diene block copolymers, and star copolymers. the VII's may also be multifunctional from the perspective of offering secondary lubricant performance features such as additional dispersancy. VII's can be present in the amount of up to 15 vol%, more preferably in the amount of up to 13 vol%, most preferably in the amount of up to 10 vol%.

[0024] Lubricating oil additives are described generally in "Lubricants and Related Products" by Dieter Klamann, Verlag Chemie, Deerfield, Fla., 1984, and also in "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith, 1967, pages 1-11, the disclosures of which are incorporated herein by reference.

[0025] The present invention is further described in the following non-limiting examples and comparative examples.

EXPERIMENTAL

A. Lab Nitration Screener Test Results

[0026] A lab nitration screener test was used to assess the oil life performance of various oil compositions. The test results identify a number of parameters including oil viscosity increase, oxidation, and nitration. All measurements are reported on a relative basis (unless otherwise indicated) so that results greater than unity represent greater levels of degradation. Numerically lower relative results represent a measure of longer oil life. In each test, a Reference Oil is tested and results are reported as a ratio of the result for the test oil divided by the result for the Reference Oil. Thus, if a tested oil has an oxidation result of 1.0, then it has oxidation performance equal to that of the Reference Oil. If the tested oil has an oxidation result less than 1.0, then the tested oil demonstrates oxidation performance superior to that of the Reference Oil

EXAMPLES AND COMPARATIVE EXAMPLES

- [0027] In the Examples, the base oil in all cases was a heavy Group II
5 basestock. Comparative Oil 1, Reference Oil 1 and Examples 1 and 2 contained
the same viscosity index improver (VI). Comparative Oil 2 is a current
commercial oil based solely on API Group II basestocks. Reference Oil 1 and
Example Oils 1 and 2 each contained the same mixture of neutral and overbased
metallic detergents, ashless dispersant, ZDDP, pour point depressant, metal
10 passivator and antifoamant. Reference Oil 1, however, employed a phenolic
antioxidant whereas the oils of Examples 1 and 2 employed a trinuclear
molybdenum compound, $\text{Mo}_3\text{S}_7(\text{DTC})_4$, and a mixture of a trinuclear
molybdenum compound, $\text{Mo}_3\text{S}_7(\text{DTC})_4$, and an ashless dihydrocarbyl
thiocarbamoyl, $(\text{S}_2\text{CNR}_2)_2\text{CH}_2$, respectively. Comparative Oil 1 used a
15 commercially available gas engine oil additive package, Oloa 1255 sold by
Chevron Chemical Company. Oloa 1255 is one of the most widely sold gas
engine oil packages and therefore represents a "benchmark standard" against
which other engine oil formulations may be measured.
- 20 [0028] The results show that the oils of the present invention, Examples 1 and
2, provided superior performance to both of the Comparative oils and the
Reference Oil, in terms of reduced oxidation, nitration and viscosity increase.
The invention examples provided superior oil life despite the absence of
conventional aminic and phenolic antioxidants. The small negative normalized
25 viscosity increase values for the invention examples simply reflect that there was
no significant change in viscosity, unlike the Comparative and Reference oils.

TABLE 1

	Comparative Oil 1	Reference Oil 1	Example 1	Example 2	Comparative Oil 2
<u>Component (vol%)</u>					
Group II basestock	87.90	90.00	90.00	90.00	-----
NGEO commercial additive package	9.6	-----	-----	-----	-----
VI					-----
Phenolic antioxidant	1.00	1.00			-----
Moly trimer	-----	-----	1.00	1.00	-----
Ashless dihydrocarbyl thiocarbamoyl	-----	-----	-----	0.50	-----
Balance of additives	1.00	9.00	9.00	9.00	-----
Commercial Oil	-----	-----	-----	-----	100.00
<u>Properties</u>					
KV, cSt @ 100°C	13.25	13.14	13.20	13.13	13.51
<u>Test Results</u>					
Nitration Screener Test					
Oxidation (relative)	1.76	1.00	0.86	0.79	1.57
Nitration (relative)	1.55	1.00	1.15	0.91	1.48
Viscosity Increase (relative)	1.70	1.00	- 0.16	- 0.12	0.73